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Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms

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Abstract

We have investigated the formation and early growth of atmospheric secondary aerosol particles building on atmospheric measurements. The measurements were part of the QUEST 2 campaign which took place in spring 2003 in Hyytiälä (Finland). During the campaign numerous new aerosol particle formation events occurred of which 15 were accompanied by gaseous sulphuric acid measurements. Our detailed analysis of these 15 events is focussed on nucleation and early growth (to a diameter of 3 nm) of fresh particles. It revealed that new particle formation seems to be a function of the gaseous sulphuric acid concentration to the power from one to two. The former would be consistent with the recently developed activation theory while the latter would be consistent with the kinetic nucleation theory. We find that some events are dominated by the activation mechanism and some are dominated by the kinetic mechanism. Inferred coefficients for the two nucleation mechanisms are correlated with the product of gaseous sulphuric acid and ammonia concentrations. This indicates that besides gaseous sulphuric acid also ammonia has a role in nucleation. Early growth of fresh particles to a diameter of 3 nm has a mean rate of 1.2 nm/h and is clearly correlated with the gaseous sulphuric acid concentration.

1 Introduction

Atmospheric aerosol particles affect the quality of our life in many different ways. In polluted urban environments, aerosols influence human health and deteriorate visibility (e.g. Donaldson et al., 1998; Stieb et al., 2002; Cabada et al., 2004). In regional and global scales, aerosol particles have a potential to change climate patterns and hydrological cycle (Ramanathan et al., 2001; Sekiguchi et al., 2003; Lohmann and Feichter, 2005). Better understanding of the various effects by atmospheric aerosols requires detailed information on how different sources and transformation processes modify aerosol properties. An important phenomenon in this regard is atmospheric aerosol

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formation, which involves the production of nanometer-size particles by nucleation and their growth to detectable sizes (Kulmala, 2003).

Atmospheric aerosol formation followed by growth up the 50–200 nm size range has been observed commonly in the continental boundary layer. Such observations cover the boreal forest region (Mäkelä et al., 1997; Kulmala et al., 1998, 2001a; Vehkamäki et al., 2004), remote continental sites (Weber et al., 1997; Birmili et al. 2003), industrialised agricultural regions (Birmili and Wiedensohler, 1998), urban and suburban areas (Väkevä et al., 2000; Stanier et al., 2004; Stolzenburg et al., 2005), and heavily-polluted environments (Dunn et al., 2004; Wehner et al., 2004; Laaksonen et al., 2005; Mönkkönen et al., 2005). Aerosol formation has also been observed in coastal environments around Europe (O'Dowd et al., 1999). A recent overview has summarised the formation and growth properties in a global point of view (Kulmala et al., 2004a), quantifying especially the formation and growth rates of nucleation events, where available.

Sulfuric acid is a key component in atmospheric aerosol formation. Several nucleation mechanisms, including binary, ternary and ion-induced nucleation, are likely to involve sulphuric acid (e.g. Bernd et al., 2005; Korhonen et al., 1999; Kulmala, 2003; Kulmala et al., 2004a; Laakso et al., 2004a). Some, if not the major, fraction of the particle growth can be explained by sulphuric acid condensation, especially in the smallest particle sizes (Kulmala et al., 2004b; Zhang et al., 2004; Boy et al., 2005; Fiedler et al., 2005; Smith et al., 2005). Sulphuric acid might also play a role in the so-called activation process, in which stable clusters containing sulphuric acid molecules will be activated for growth (Kulmala et al., 2005b). It is therefore important to measure sulphuric acid concentrations and aerosol relevant parameters at the same time in order to quantify the contribution of sulphuric acid to both particle formation and growth.

The present study was inspired by the observation that on new particle formation days, the temporal evolution of the number concentration of nucleation mode particles seems to follow the concentration of sulphuric acid. In view of this, we reanalysed the data from the measurement campaign QUEST 2. The main goal of the QUEST-project

(Quantification of Aerosol Nucleation in the European Boundary Layer) has been the qualitative and quantitative analysis of particle nucleation and growth in three European regions. During the QUEST 2 campaign in Hyytiälä (17 March to 13 April 2003), sulphuric acid concentrations and particle number size distributions were measured continuously on 23 days. From these data various quantities, such as the formation and growth rate of aerosol particles, were calculated.

The general goal of this study is to get information about the aerosol formation processes below 3 nm diameter, which is the lower limit of current instruments for measuring neutral atmospheric particles. More specifically, we aim to address the following questions: i) how sulphuric acid and nucleation mode particle concentrations are related to each other, ii) how large is the particle growth rate from 1 to 3 nm and what is the reason for its variability, iii) which particle formation mechanism explains the measurement data best, and iv) how large are relevant activation/kinetic constants associated with the different particle formation mechanisms and how the values of these constants vary as a function of measured parameters? The investigation is based on analysis of observed data. The particle growth rate from 1 to 3 nm will be estimated from the observed time shift between increasing sulphuric acid and ultrafine particles number concentration. Two different particle formation mechanisms will be tested, the recently-developed activation theory (Kulmala et al., 2005b) and kinetic (barrierless) nucleation theory (McMurry and Friedlander, 1979; Lushnikov and Kulmala, 1998).

2 Materials and methods

2.1 Measurements

We utilized the data set of QUEST 2 (Quantification of aerosol nucleation in the European boundary layer) campaign that was held at the SMEAR II station in Hyytiälä, Finland, during 18 March–9 April 2003. The QUEST 2 data set is quite unique in the sense that during the campaign a large number of events was observed: of the total

of 23 measurement days 20 were new particle formation days. During QUEST 2 campaign a large number of different quantities were measured; here we describe only the measurements relevant to this study.

The measurement station SMEAR II (Station for Measuring Forest Ecosystem – Atmosphere Relations) is located in Southern Finland (61°51′ N, 24°17′ E, 181 m a.s.l.) in a rural region with large areas of forested land. The conditions at the station are most of the time relatively clean, even though polluted continental air arrives occasionally from the south-west to south-east directions. Also the nearest city, Tampere, located 60 km south-west from the station, can influence the local air quality. More information about the station and the measurement equipment can be found in Hari and Kulmala (2005) and at http://www.atm.helsinki.fi/SMEAR/.

Particle number size distributions of atmospheric aerosol particles from 3 to 500 nm were measured continuously, with 10-min time resolution, by a DMPS (Differential Mobility Particle Sizer) setup. The setup consists of two parallel differential mobility analyzers (DMAs) that classify particles in size ranges 3–10 nm and 10–500 nm, the total number of size classes being 32. DMPS setup is described in more detail in e.g. Laakso et al. (2004a).

The sulphuric acid concentration was measured by a chemical ionization mass spectrometer (CIMS) built by the MPI-K Heidelberg (see Hanke et al., 2002). The time resolution of the spectrometer was less than 1 s, but the data was averaged over 60 s in order to reduce statistical error. The sulphuric acid detection limit was 1×10^5 cm^{-3} and the relative measurement error 30%.

Temperature, relative humidity and concentrations of trace gases (O_3, NO_x, SO_2) are measured continuously at SMEAR II station (see Kulmala et al., 2001a). Ammonia and monoterpene concentrations were measured during the campaign as described in details by Janson et al. (2001), and OH concentrations were estimated using the method described by Boy et al. (2005).

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2.2 Data analysis

2.2.1 Estimation of particle formation rates from the DMPS data

In this study, we focus on the freshly-nucleated particles and their relation to the sulphuric acid concentration. From the DMPS data we consider the size range 3–6 nm that covers the four lowest DMPS channels. This size range is small enough to be considered as freshly nucleated but still large enough to achieve a relatively good statistics and reduce the influence of measurement uncertainties present in lowest DMPS channels. The particle number concentration in this 3–6 nm size range is denoted by N_{3-6}.

The time evolution of N_{3-6} is described with a balance equation

$$\frac{dN_{3-6}}{dt} = GR_{3\,\mathrm{nm}} \cdot n_{3\,\mathrm{nm}} - GR_{6\,\mathrm{nm}} \cdot n_{6\,\mathrm{nm}} - CoagS_{3-6} \cdot N_{3-6}, \quad (1)$$

including terms for growth into the 3–6 nm range over the 3 nm barrier, out of the range over the 6 nm barrier and loss by coagulation scavenging. Here, GR denotes particle growth rate, and the function n is a particle size distribution function, defined as $n=dN/dd_p$ with d_p=particle diameter. $CoagS_{3-6}$ denotes the average coagulation sink for the 3–6 nm range (Kulmala et al., 2001b). By rearranging the terms, and denoting the first term on the right hand side of Eq. (1) by J_3, the following equation is obtained:

$$J_3 = \frac{dN_{3-6}}{dt} + CoagS_{d_p=4\,\mathrm{nm}} \cdot N_{3-6} + \frac{1}{3\,\mathrm{nm}} GR \cdot N_{3-6}. \quad (2)$$

J_3 is the apparent nucleation rate, i.e. the formation rate of new particles into the measurable range of above 3 nm. Here the coagulation loss (last term on the right hand side of Eq. 1) for the interval 3–6 nm has been approximated by a term representing loss of 4 nm sized particles, directly and easily calculated from the measured background particle size distribution, with hygroscopicity effects estimated as in Laakso et al. (2004b). The third term representing condensation loss out of the size range 3–6 nm comes from approximating $n_{6\,\mathrm{nm}}$ and $GR_{6\,\mathrm{nm}}$ by N_{3-6}/(6 nm–3 nm) and GR, respectively. Here

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GR is estimated from measured *GR* as explained in Sect. 2.2.2. The first term on the right hand side of Eq. (2), the change in the 3–6 nm particle number concentration, is directly obtained from the DMPS measurements.

The magnitude of the coagulation loss term relative to the term dN_{3-6}/dt in Eq. (2) depends strongly on the magnitude of the coagulation sink: with small coagulation sink values it has an effect of the order of 10% or less but with large coagulation sink values the correction can be of the same order or greater than the term dN_{3-6}/dt. The last term is negligible at the beginning of the event, but at later stages may become of same order as dN_{3-6}/dt.

2.2.2 Time shift analysis: growth rate GR_{1-3} and correlation of N_{3-6} and $[H_2SO_4]$

There is quite a vast consensus in the scientific community that sulphuric acid is participating in the formation of new particles in some way. This is supported by the observed close connection between concentrations of sulphuric acid and small particles: during nucleation events an increase in the concentration of small particles is often preceded by an increase in sulphuric acid concentration. This time delay Δt between the rise in sulphuric acid and particle number concentration can be interpreted as the time it takes for the clusters to grow from the nucleated size of ~1 nm to the detectable size of 3 nm in diameter. Based on this assumption the growth rate from 1 nm to 3 nm can be estimated as:

$$GR_{1-3} = \frac{2\ \text{nm}}{\Delta t}\ . \tag{3}$$

This method to determine growth rate of freshly nucleated particles may be termed "time-shift analysis" and it has been used previously by Fiedler et al. (2005) in connection with the QUEST 2 campaign. Here we extend this concept in such a way that also the correlation of number concentration of small 3–6 nm particles (N_{3-6}) and sulphuric acid ($[H_2SO_4]$) is investigated so that the time delay between them is taken into account.

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In this study, it was noticed soon that there exist two types of correlations between N_{3-6} and H_2SO_4 concentration: on some days N_{3-6} follows the shape of $[H_2SO_4]$ curve while on other days N_{3-6} correlates clearly with $[H_2SO_4]^2$. Therefore, on some days the time delay Δt was taken between the N_{3-6} and $[H_2SO_4]$ curves and on other days between the N_{3-6} and $[H_2SO_4]^2$ curves. Regardless of the prevailing relationship between N_{3-6} and $[H_2SO_4]$, the interpretation of Δt as growth time from ~1 nm to 3 nm stays the same.

The investigation of the relationship between particle concentration N_{3-6} and sulphuric acid was started by determining the time lag (delay) between increase in concentrations N_{3-6} and $[H_2SO_4]$. When this time lag was taken into account by delaying the $[H_2SO_4]$ curve by Δt, the correlation of N_{3-6} and $[H_2SO_4]$ became very clear. The correlation was examined both by visually investigating the N_{3-6} and $[H_2SO_4]$ curves and by calculating correlation coefficients for N_{3-6} and $[H_2SO_4]$ or $[H_2SO_4]^2$. All event days were classified according to which type of correlation – with $[H_2SO_4]$ to the power of 1 or 2 – was prevailing.

There is a close interplay between the determination of the time delay Δt and the type of correlation of N_{3-6} and $[H_2SO_4]$. If the time delay is taken between N_{3-6} and $[H_2SO_4]$ curves we get typically a different value than if the time delay is taken between N_{3-6} and $[H_2SO_4]^2$. Furthermore, we may get different values for Δt if we consider only the first rise of the curves or look at the time lag between the whole curves. For these reasons, there may be subjectivity or at least variation in the determination of the time lag between different persons, especially on days when there are some interfering processes present e.g. due to changing air mass. In this study, the value for the time delay was determined both by looking the first rise of the N_{3-6} and $[H_2SO_4]$ or $[H_2SO_4]^2$ curves and the form of the curves during the whole event.

2.2.3 Atmospheric nucleation rates

If the formation rate of 3 nm particles J_3 is known, the nucleation rate J_1 at time $t = t' - \Delta t$ can be estimated using the method presented by Kerminen and Kulmala (2002):

$$J_1(t) = J_3(t') \exp\left(\gamma \frac{CS'}{GR} \left(\frac{1}{1\,\mathrm{nm}} - \frac{1}{3\,\mathrm{nm}}\right)\right) . \quad (4)$$

Here CS' is condensation sink (in units m^{-2}), GR is the growth rate (in nm/h) and γ is a coefficient with a value of about $0.23\,\mathrm{m}^2\,\mathrm{nm}^2\,\mathrm{h}^{-1}$.

Thus we first estimate the formation rate of 3 nm partices (J_3) from the DMPS measurement data using Eq. (2) and then the nucleation rate of ~1 nm particles $J_1(t)$ from Eq. (4). For the condensation sink CS' we use the median value from the interval $[t, t+\Delta t]$.

A correlation between N_{3-6} and $[H_2SO_4]$ or $[H_2SO_4]^2$ suggests that sulphuric acid is participating in nucleation in some way. Using J_1 and J_3 estimated from the particle measurement data we test two hypothetic nucleation mechanisms that should have a power law dependence of the sulphuric acid concentration.

The first nucleation mechanism to be tested we call "activation type nucleation" and it is directly proportional to the sulphuric acid concentration. This mechanism was recently proposed by Kulmala et al. (2005b). Nucleation is thought to happen as activation of small clusters containing one sulphuric acid molecule via e.g. heterogeneous nucleation or heterogeneous chemical reactions. Because critical clusters are assumed to contain one sulphuric acid molecule, nucleation rate is directly proportional to sulphuric acid concentration. We do not make any assumptions of the specific growth mechanism or vapours participating in the cluster activation process, but express the nucleation rate simply by (Kulmala et al., 2005b):

$$J_1 = A\ [H_2SO_4]\,, \quad (5)$$

where the coefficient A will be determined according to measurement data. This activation coefficient A contains the physics and chemistry of the nucleation process;

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however, so far it is merely an empirical coefficient. Studying the variation of A and its dependencies on different quantities can give us information of details of the nucleation process.

The second nucleation mechanism to be tested has the functional form of kinetic nucleation of molecules containing sulphuric acid, i.e. it is proportional to the square of sulphuric acid concentration. This mechanism we call "kinetic type nucleation". In kinetic nucleation, critical clusters are formed by collisions of sulphuric acid molecules or other molecules containing sulphuric acid, e.g. ammonium bisulphate molecules. The upper limit for kinetic nucleation, so called "kinetic limit", is set by the collision rate of molecules given by kinetic theory of gases. Here we let the collision frequency function be a free parameter and calculate nucleation rate as:

$$J_1 = K\ [H_2SO_4]^2\,, \tag{6}$$

where the coefficient K will be adjusted to fit J_1 calculated from particle measurement data. This kinetic coefficient K contains again the details of the nucleation process, specifically the probability that a collision of two sulphuric acid containing molecules results in the formation of a stable critical cluster.

The nucleation coefficients A and K are determined as follows. From measurement data we get J_3 using Eq. (2) and from that nucleation rate J_1 is calculated by using the Eq. (4). Then we calculate the nucleation rate J_1 from the measured sulphuric acid concentration according to the two hypothetic nucleation mechanisms, activation type and kinetic type nucleation (Eqs. 5 and 6). These nucleation rates are further scaled to formation rates of 3 nm particles using Eq. (4) in the opposite direction than above. Now we have two quantities to compare: J_1 estimated from measured particle concentrations and J_1 calculated from sulphuric acid concentration, and similarly, J_3 calculated from measured particle concentrations and J_3 estimated from nucleation rates calculated from sulphuric acid concentration. By comparing the J_1 curves with each other we search for the values for the coefficients A and K that give the best agreement with the J_1 estimated from particle measurements. In the same way we

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compare the J_3 curves, to double-check the values of A and K. The comparison of J_1 and J_3 curves is done only visually, because in that way the essential features can be simply picked up to be taken into account, and some interfering peaks in the data due to e.g. changing air mass can be left out from the analysis. Computational fitting methods, such as calculation of correlation coefficients, would not work here well because of quite big variations present in the J_1 and J_3 data. Furthermore, in the first place we want to get an order of magnitude information about the nucleation coefficients and the exact numerical values are not crucial, so the use of computational fitting methods would be dispensable.

3 Results and discussion

During QUEST 2 campaign new particle formation was observed to occur on 20 days of the total of 23 measurement days. For some event days the sulphuric acid data was missing, and for this analysis we had the data on 15 particle formation days.

3.1 Correlation of N_{3-6} and sulphuric acid

On all 15 days that were analysed the number concentration in size range 3–6 nm (N_{3-6}) and sulphuric acid concentration were clearly correlated. On some days N_{3-6} correlated with $[H_2SO_4]$ but on other days the N_{3-6} curve had a similar shape as the $[H_2SO_4]^2$ curve. Figure 1a presents an example of direct correlation between N_{3-6} and $[H_2SO_4]$ observed on day 84 (25 March 2003); the surface plot for the event is shown in Fig. 1b. From Fig. 1a it is clearly seen, that the forms of the N_{3-6} and $[H_2SO_4]$ curves are almost identical during the particle formation event that spans approximately from 07:00 a.m. to 07:00 p.m. (84.3–84.8 in days). However, there is a time lag between the curves arising from the time required for the nucleated clusters to grow to size of 3 nm detectable by DMPS. In the lower panel of Fig. 1a the $[H_2SO_4]$ curve has been delayed by time shift Δt=1.4 h, and in this figure the direct correlation between N_{3-6}

and $[H_2SO_4]$ is even more evident.

Figures 2a and b present an example of a day when N_{3-6} correlates with the square of $[H_2SO_4]$. The upper panel of the Fig. 2a shows that N_{3-6} and $[H_2SO_4]$ are somewhat related to each other, but they are not directly correlated even if the time lag between the curves was taken into account. However, when we plot the square of $[H_2SO_4]$ and delay it by Δt=1.2 h, it coincides well with the N_{3-6} curve. It is worth noting that the correlation between N_{3-6} and $[H_2SO_4]$ or N_{3-6} and $[H_2SO_4]^2$ stays the same during the whole nucleation event, not only in the start of the event when the time lag is visible. This implies that the growth rate from 1 to 3 nm is relatively constant the whole day.

The time delays and types of correlation – N_{3-6}~$[H_2SO_4]$ or N_{3-6}~$[H_2SO_4]^2$ – were determined for all 15 days. From the time delay Δt the growth rate from nucleated size of ~1 nm to detectable size of 3 nm, GR_{1-3}, was calculated by Eq. (3). The results are collected in Table 1. The time delay varied between 1.0 and 4.1 h with a mean value of 2.0 h, median of 1.7 h and standard deviation of 0.9 h. After omitting the two largest values on days 90 and 93, the standard deviation of Δt was considerably smaller (0.5 h) and mean value changed to 1.7 h while median stayed the same. The growth rates corresponding to these time delays were in the range 0.5–2.1 nm/h with mean and median of 1.2 nm/h and standard deviation of 0.5 nm/h. The reason for the same mean and median values of GR_{1-3}, as opposed to the different mean and median of Δt, is that in the GR_{1-3} formula Δt is in the denominator. In case of GR_{1-3}, omitting the days 90 and 93 from the data set had only a minor influence to mean, median and standard deviation, which again was due to the fact that Δt is in the denominator.

The fraction of the growth rate GR_{1-3} that could be explained by the condensation of sulphuric acid can be estimated by comparing GR_{1-3} to the growth rate calculated from the sulphuric acid concentration. This latter can be calculated from (Kulmala et al., 2001b):

$$GR = \frac{d\,d_p}{dt} = \frac{4\,\beta_M\,M_{H_2SO_4}\,D_{H_2SO_4}\,C_{H_2SO_4}}{\rho\,d_p}\,, \tag{7}$$

where M_{H2SO4} is the molecular mass of sulphuric acid, D_{H2SO4} is its diffusion coefficient, C_{H2SO4} is its concentration, ρ is the particle density and β_M is the Fuchs-Sutugin transitional correction factor. This equation is derived for spherical nucleation mode particles from macroscopic condensation theory, and these assumptions do not hold anymore for 1–3 nm sized particles. Lehtinen and Kulmala (2003) have considered condensation with a molecular resolution and found that condensation is enhanced at small particle sizes compared with the macroscopic treatment. According to calculations made with an aerosol dynamic model UHMA (Korhonen et al., 2004), the condensation rate is enhanced by a factor between 2 and 3 compared with the value obtained by Eq. (7) for 1–3 nm particles. According to Eq. (7) with a condensation enhancement factor of 2.5, sulphuric acid can explain typically about 50% of the growth rate from 1 to 3 nm, but on three days even over 70% (see Fig. 3). As seen from Fig. 3, the contribution of sulphuric acid to the particle growth increases, on average, with increasing sulphuric acid concentration. Exact numbers about the contribution of sulphuric acid cannot be given, but these estimations reveal that on some days sulphuric acid may be responsible for main part of the particle growth from 1 to 3 nm. However, sulphuric acid alone cannot explain the growth on all days.

The relation between N_{3-6} and $[H_2SO_4]$ followed the pattern N_{3-6}~$[H_2SO_4]$ on six days and pattern N_{3-6}~$[H_2SO_4]^2$ on five days. On four days it was not possible to say which of the two relations was better (see Table 1). The judgement on the type of the correlation was based on both visual perception and correlation coefficients. On some days there were some interfering peaks in the data that were clearly due to some other phenomenon than the chain "nucleation-growth-observation in 3–6 nm". For those days the correlation coefficient was calculated only for that part of the data where the correlation between N_{3-6} and $[H_2SO_4]$ was clear; this is indicated by an asterisk in the Table 1. For other days the correlation coefficients were calculated using the whole data. However, also in that case the event period contributes the most to the correlation coefficient because concentrations are highest during the event. On all days (except day 94) the correlation coefficient for the prevailing correlation –

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N_{3-6}~$[H_2SO_4]$ or N_{3-6}~$[H_2SO_4]^2$ – was greater than 0.79, and on six days even over 0.9. This demonstrates that the correlation between N_{3-6} and $[H_2SO_4]$ or $[H_2SO_4]^2$ is remarkably strong on most days.

The overall relation between N_{3-6} and $[H_2SO_4]$ is shown in Fig. 4, in which the logarithm of N_{3-6} is plotted versus the logarithm of $[H_2SO_4]$. Here we have included the data during events; the data in early morning and late night is left out because at those times both sulphuric acid concentration and N_{3-6} are low and there is no new particle formation. The chosen time interval varies between the days, but most often it is the period from 06:00 a.m. to 06:00 p.m. In this scatter plot, the slope tells the exponent in the correlation N_{3-6}~$[H_2SO_4]^x$. From Fig. 4 it can be clearly seen that the exponent x lies somewhere between 1 and 2. However, separate cases with the exponent 1 and 2 could not be distinguished from the scatter plot, as was done in the day-by-day comparison of the N_{3-6} and $[H_2SO_4]$ curves, since in the scatter plot points from different days are mixed together. A least squares fit to the data gives 1.24 for the exponent, representing an average value for the exponent in the entire 15-day data set.

3.2 Testing different nucleation mechanisms

The formation rate of 3 nm particles (J_3) was calculated from particle measurements using Eq. (2) and scaled to the estimated nucleation rate J_1 using the formula (4). These formation rates are referred to as "measured" henceforth. In order to test the two hypothetic nucleation mechanisms, "activation type" and "kinetic type" nucleation, we calculated the nucleation rate J_1 from measured sulphuric acid concentration assuming a linear or square dependence on the sulphuric acid concentration. The coefficients A and K in Eqs. (5) and (6) were free parameters that were adjusted to fit the "measured" nucleation rates. Furthermore, we used the formula (4) to convert the "activation type" and "kinetic type" nucleation rates J_1 into the formation rate J_3 which then could be compared with the "measured" J_3 estimated from DMPS data.

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An example of "measured" nucleation rate compared with the ones calculated from sulphuric acid concentration according to "activation" and "kinetic" hypotheses is shown in Fig. 5. The values of activation and kinetic coefficients (A and K) were adjusted so that during nucleation event the agreement was best. For this day (day 85) it seems that the "activation type" nucleation works better than the "kinetic type" nucleation, although the difference between these two is not very large. Figure 6 shows an example of a day (day 91) when the kinetic nucleation theory seems to work slightly better.

The same kind of visual fitting of the parameters A and K, as presented in Figs. 5 and 6, was made for all 15 event days. The resulting values of A and K are summarized in Table 2. Although the nucleation rates vary quite much from day to day, the coefficients A and K lie approximately within a range of a factor of ten. For the activation coefficient we got values between 0.4×10^{-6} and $6.0\times10^{-6}\,s^{-1}$ with a mean of $1.7\times10^{-6}\,s^{-1}$ and median of $1.0\times10^{-6}\,s^{-1}$. The kinetic coefficient had even a smaller variability with a minimum value of $0.2\times10^{-12}\,cm^3\,s^{-1}$, maximum of $1.4\times10^{-12}\,cm^3\,s^{-1}$, mean of $0.6\times10^{-12}\,cm^3\,s^{-1}$ and median of $0.5\times10^{-12}\,cm^3\,s^{-1}$. For comparison, a kinetic coefficient for collisions of two H_2SO_4 molecules is about $3\times10^{-10}\,cm^3\,s^{-1}$ assuming perfect sticking and energy transfer. On the other hand, a typical (in upper range) chemical reaction rate coefficient in the gas phase is of the order of 10^{-14}–$10^{-12}\,cm^3\,s^{-1}$. This means actually that both coefficients – activation and kinetic – are of the same order as chemical reaction rate coefficients in the gas phase assuming that the concentrations of vapours participating in activation are around 10^6–$10^8\,cm^{-3}$.

For most days it was hard to say reliably whether "activation type" or "kinetic type" nucleation was better as was done when examining the correlation of N_{3-6} and $[H_2SO_4]$. Therefore we determined both coefficients A and K for all days, and at this stage make no conclusion on specific nucleation mechanism on a specific day. An overall picture about the relation is seen from Fig. 7, in which the logarithm of J_1 estimated from particle measurements is plotted against the logarithm of $[H_2SO_4]$ for the whole campaign. Activation type dependency between J_1 and $[H_2SO_4]$ should appear in the plot as a line with slope 1 and kinetic type dependency as a line with slope 2. However, as was

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the case with N_{3-6} and $[H_2SO_4]$, the points from different days are mixed and we can only say that in relationship $J_1 \sim [H_2SO_4]^x$ the exponent is something between 1 and 2. On average, the data points to activation type nucleation: a least squares fit to the whole data gives 1.16 for the exponent. The corresponding plot for J_3 and sulphuric acid is presented in Fig. 8, and similarly J_3 correlates with $[H_2SO_4]^x$ with exponent x between 1 and 2.

It should be noted, that even though the relation between N_{3-6} and sulphuric acid was on day 85 $N_{3-6} \sim [H_2SO_4]^2$, i.e. with exponent 2, for nucleation the activation formula (Eq. 5) with direct correlation $J_1 \sim [H_2SO_4]$ appears to fit better (see Figs. 2a and 5). Thus the exponents of the correlation $N_{3-6} \sim [H_2SO_4]^x$ listed in Table 1 should not be interpreted as exponents of the nucleation formula. There are several possible reasons for the change in exponent from 1 to 2 when going from correlation $J_1 \sim [H_2SO_4]^x$ to $N_{3-6} \sim [H_2SO_4]^x$. If sulphuric acid makes the main part of the growth from 1 to 3 nm, it may cause another $[H_2SO_4]$-dependency to N_{3-6} in addition to linear dependency in nucleation. Also some organic vapours formed in oxidation reactions with OH radical can have approximately the same pattern than sulphuric acid, which itself is formed in reactions with OH, and thereby they may cause an apparent correlation of N_{3-6} with $[H_2SO_4]^2$. Similar apparent relation with $[H_2SO_4]$ may be caused also by condensation sink, which decreases in the morning due to dilution of background aerosol when boundary layer develops, and can have a pattern similar to inverse of [OH].

During the QUEST 2 campaign there were three days (days 81, 89 and 95) when no new particle formation was observed. On day 95 sulphuric acid measurements were made, so we can test how large particle formation rates would be expected according to the "activation type" and "kinetic type" nucleation pathways. For the growth rate GR_{1-3} and coefficients A and K, median values from the campaign were used. The resulting nucleation rate (J_1) was very low, always smaller than 1 $cm^{-3}\,s^{-1}$. The formation rate of 3 nm particles (J_3) was naturally even smaller, always below 0.1 $cm^{-3}\,s^{-1}$. These formation rates are too small to cause a new particle formation event. Thus also data from this non-event day fits in the framework of "activation type" or "kinetic

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type" nucleation with coefficients A and K estimated from fittings to data on particle formation days.

3.3 Correlations of the growth rate GR_{1-3} and nucleation coefficients A and K with other quantities

In order to get more information on the particle growth mechanism from 1 to 3 nm as well as on the nucleation mechanism behind used formulas for nucleation rate (Eqs. 5 and 6), we searched for correlations of the growth rate (GR_{1-3}) and nucleation coefficients (A and K) with several other quantities. Our aim was to find out whether there are quantities that could explain the variation of GR_{1-3}, A and K from day to day. The daytime values, averaged over the period 09:00 a.m.–03:00 p.m., of the following measured quantities were considered: temperature, relative humidity, condensation sink, and the concentrations of sulphuric acid, monoterpenes and ammonia. In addition, correlations with the quantities [OH]×[terp]/CS and [O_3]×[terp]/CS, representing the proxies for condensable organic vapours, were investigated.

As already shown in Fig. 3, GR_{1-3} correlated nicely with sulphuric acid concentration. It was the only significant correlation found for GR_{1-3} (correlation coefficient 0.8). Correlations for nucleation coefficients A and K are presented in Table 3. Temperature, sulphuric acid and ammonia had no significant correlation with the coefficients A and K, whereas condensation sink, relative humidity and proxies for condensable organic vapours had a negative correlation. More specifically, there was a positive correlation for A and K with the inverses of these quantities, i.e. 1/CS, 1/RH, CS/([OH]×[terp]) and CS/([O_3]×[terp]). This means that when more terpene oxidation products were present, the values of A and K needed for reproducing the observed new particle formation rates were smaller. It further means that both "activation type" and "kinetic type" nucleation processes seem to depend on the concentration of oxidation products of terpenes, being more effective at higher concentrations. The coefficient for "kinetic type" nucleation, K, had a stronger correlation with CS/([OH]×[terp]) and CS/([O_3]×[terp]) than did the coefficient for "activation type" nucleation, A.

We tested also correlations with some products of the quantities mentioned above. Interestingly, A and K seemed to correlate with $[H_2SO_4]\times[NH_3]$ even if there was no significant correlation with sulphuric acid or ammonia alone. The correlation coefficients of A with $[H_2SO_4]$ and $[NH_3]$ were 0.42 and 0.25, respectively, and those of K with $[H_2SO_4]$ and $[NH_3]$ were 0.17 and 0.3, respectively. However, correlation coefficients with $[H_2SO_4]\times[NH_3]$ were considerably greater: 0.66 for A and 0.62 for K. This correlation suggests that both sulphuric acid and ammonia are important in new particle formation. The higher the sulphuric acid and ammonia concentrations, the larger are nucleation coefficients. This means that in case of activation type nucleation, a larger fraction of sulphuric acid molecules gets activated to 3 nm size, and in case of kinetic type nucleation, a larger fraction of collisions of two molecules containing sulphuric acid leads to formation of permanent clusters.

Although the correlations found are very promising, we should keep in mind that the used dataset was rather small (10–14 days). This is due to the fact that on some analysed days a fraction of data, such as ammonia concentration, was missing. Therefore correlations found are mainly suggestive.

4 Conclusions

In this study, the close correlation between number concentration of freshly nucleated particles (3–6 nm) and sulphuric acid has been investigated in detail to analyze the formation and growth mechanism of atmospheric aerosol particles. The analysis was based on data on 15 new particle formation days observed during QUEST 2 campaign in spring 2003 in Hyytiälä (Finland). During new particle formation, the concentration of 3–6 nm particles was found to have a power-law dependence on the sulphuric acid concentration, with an exponent value 1 or 2. Using time shift analysis based on this correlation, the growth rate from 1 nm to 3 nm has been determined. The mean value was 1.2 nm/h and a large fraction of it, on average about 50%, can be explained by the condensation of sulphuric acid.

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Formation rates of 3 nm and 1 nm particles estimated from particle measurements were correlated with sulphuric acid concentration to the power from 1 to 2, showing that there are possibly couple of varying nucleation mechanisms working during the analyzed period. Recently we have presented an activation theory to describe the linear dependence between sulphuric acid concentration and atmospheric nucleation rate (Kulmala et al., 2005b). Here we tested two nucleation mechanisms corresponding to the two dependencies: "activation type" nucleation with linear dependency and "kinetic type" nucleation with square dependency on sulphuric acid. According to our analysis, both mechanisms seem to be good candidates for atmospheric nucleation. From fittings to particle measurement data empirical nucleation coefficients were determined. The mean values of the activation and kinetic coefficients were 1.7×10^{-6} s^{-1} and 0.6×10^{-12} cm^3 s^{-1}, respectively, being of the same order of magnitude as chemical reaction rate coefficients in the gas phase with vapour concentrations around 10^6–10^8 cm^{-3}.

When analyzing the dependence of activation and kinetic coefficients on other measured data, a correlation with $[H_2SO_4]\times[NH_3]$ was seen, even though there was no correlation with $[H_2SO_4]$ or $[NH_3]$ alone. Also the anticorrelation with the concentration of oxidation products of terpenes was observed, indicating that the higher their concentrations, the smaller the activation and kinetic coefficients are. Although at present only indicative, this gives a clear hint that all three gaseous precursors – sulphuric acid, ammonia and terpene oxidation products – are important in formation and growth of atmospheric aerosol particles.

Recently there has been some experimental development in finding out nucleation and growth mechanisms in atmospheric conditions (see Kulmala et al., 2005a). However, still the typical lower limit for atmospheric aerosol particle measurements is 3 nm, and the current estimates on the magnitude of regional and global secondary aerosol formation rely mainly on modelling and are subject to large uncertainties. There are uncertainties in identifying both the detailed nucleation mechanisms as well as the nucleation rates, and the formation rate of 3 nm particles depends strongly on growth rate

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from 1 to 3 nm. Analysis of the relationship between sulphuric acid and freshly formed particles gives us a tool to get information about early stages of particle formation and helps us to overcome the gap between nucleation and detection of particles at 3 nm. For this type of data analysis, it is crucial to measure particles and sulphuric acid simultaneously. To find out how broadly these types of correlations are valid, it would be essential to analyze data from different environments. In the future, we will continue the study also by aerosol dynamics modelling to deeper understand the physical phenomena behind the close correlation between the concentrations of sulphuric acid and freshly nucleated particles.

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Table 1. Time delay (Δt) between N_{3-6} and $[H_2SO_4]$ or $[H_2SO_4]^2$ and the corresponding growth rate from 1 nm to 3 nm (GR_{1-3}) for event days during QUEST 2 campaign in Hyytiälä, Finland. The fourth column indicates which correlation was better, and the last two columns the correlation coefficients (R) for correlations N_{3-6}~$[H_2SO_4]^{1 \text{ or } 2}$ with $[H_2SO_4]$ delayed by Δt. A minus sign indicates that the quantity could not be determined.

Day	Δt (h)	GR_{1-3} (nm/h)	Exponent of the correlation	R exp. 1	R exp. 2
78	2.4	0.8	–	0.57	0.55
79	1.9	1.0	2	0.70	0.82
80	2.2	0.9	2	0.90*	0.92*
82	1.7	1.2	2	0.83	0.84
84	1.4	1.4	1	0.92	0.85
85	1.2	1.7	2	0.90	0.93
87	2.4	0.8	1	0.85	0.78
88	–	–	–	–	–
90	3.6	0.6	1	0.87	0.80
91	1.2	1.7	2	0.91	0.93
92	1.2	1.7	–	0.77*	0.77*
93	4.1	0.5	2	0.95*	0.93*
94	1.7	1.2	2	0.71	0.59
96	2.4	0.8	1	0.81*	0.69*
97	1.0	2.1	1	0.79	0.66
98	1.2	1.7	2	0.93*	0.92*
Mean	2.0	1.2			
Median	1.7	1.2			
Std deviation	0.9	0.5			

* In the calculation of the correlation coefficient only a period of the day is considered during which the correlation is observable.

Table 2. Values for nucleation coefficients determined from fittings to experimental data: activation coefficient A in the formula of activation type nucleation, and kinetic coefficient K in the formula of kinetic nucleation.

Day	A (10^{-6} s^{-1})	K (10^{-12} cm^3 s^{-1})
78	0.8	0.8
79	1.0	0.5
80	6.0	1.4
82	0.9	0.4
84	0.5	0.2
85	3.0	0.7
87	0.5	0.2
88	2.0	0.6
90	–	–
91	3.0	1.0
92	3.0	1.0
93	–	–
94	1.5	0.4
96	0.4	0.2
97	1.0	0.3
98	0.8	0.3
Mean	1.7	0.6
Median	1.0	0.5
Min	0.4	0.2
Max	6.0	1.4

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Table 3. Correlation coefficients for activation and kinetic coefficients *A* and *K* with daytime averages (09:00 a.m.–03:00 p.m.) of several quantities during QUEST 2 campaign. Correlation coefficients greater than 0.5 are marked as bold.

	A R	K R	Number of data points
T	−0.25	−0.29	14
RH	**−0.52**	**−0.55**	14
$[H_2SO_4]$	0.42	0.17	14
$[NH_3]$	0.25	0.30	10
[terp]	0.07	−0.32	12
[terp]×[OH]/CS	**−0.52**	**−0.62**	12
[terp]×$[O_3]$/CS	−0.43	**−0.55**	12
CS	**0.51**	0.42	14
RH^{-1}	**0.59**	**0.61**	14
$([terp]\times[OH]/CS)^{-1}$	**0.67**	**0.80**	12
$([terp]\times[O_3]/CS)^{-1}$	**0.54**	**0.72**	12
$[H_2SO_4]\times[NH_3]$	**0.66**	**0.62**	10
GR_{1-3}	0.09	0.007	13

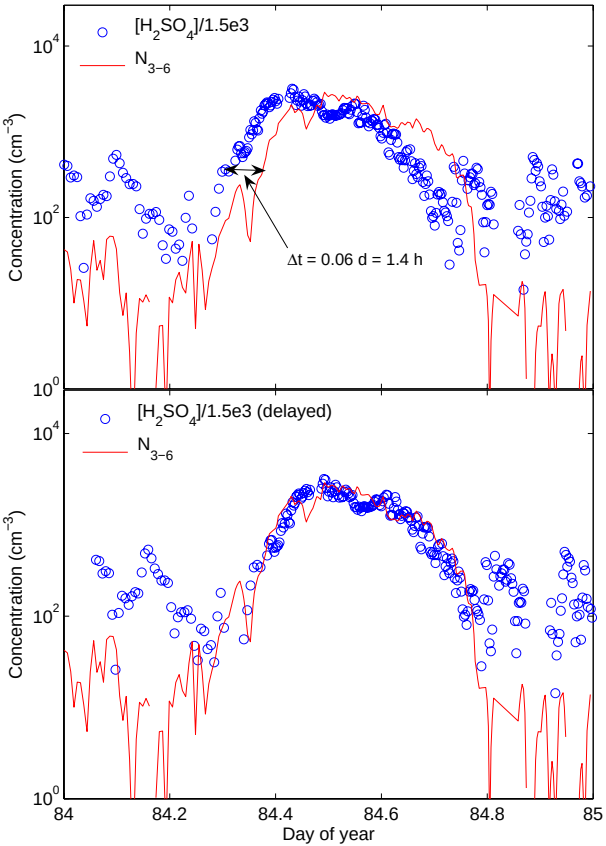

Fig. 1. (a) (upper panel) Number concentration of 3–6 nm particles (N_{3-6}) and sulphuric acid concentration (scaled) for day 84 (25 March 2003). The time shift Δt between the curves is marked by an arrow. (lower panel) N_{3-6} and $[H_2SO_4]$ delayed by the time shift Δt=1.4 h, showing excellent correspondence between N_{3-6} and $[H_2SO_4]$ during the event.

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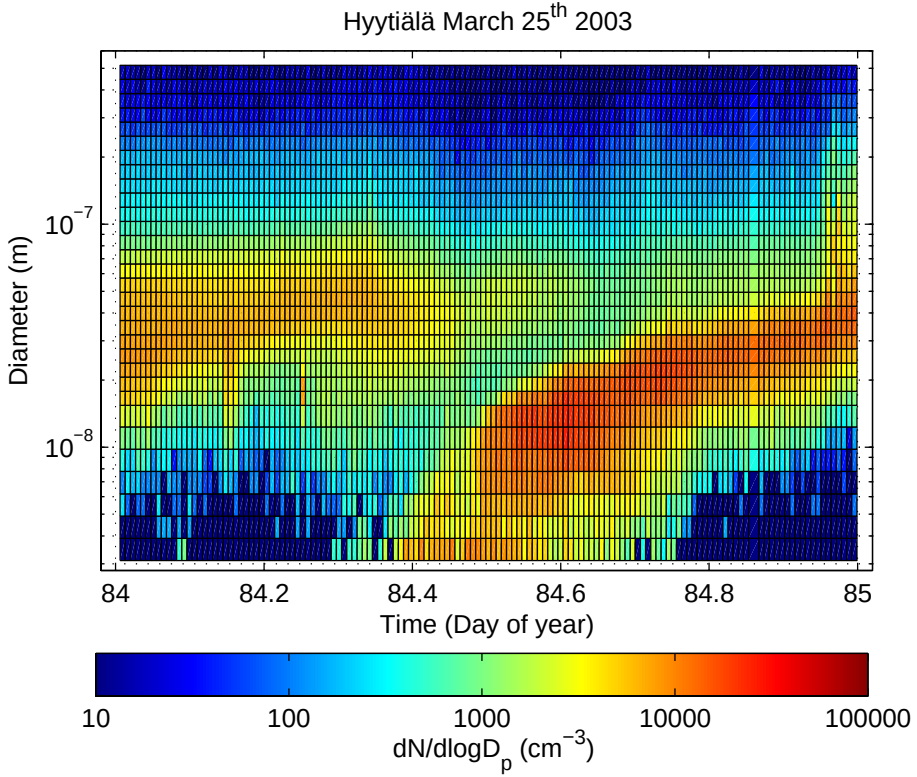

Fig. 1. (b) Surface plot showing the time evolution of particle size distribution on day 84 (25 March 2003) measured by DMPS. Time is on the x-axis, particle diameter on the y-axis and colour indicates normalized number concentration.

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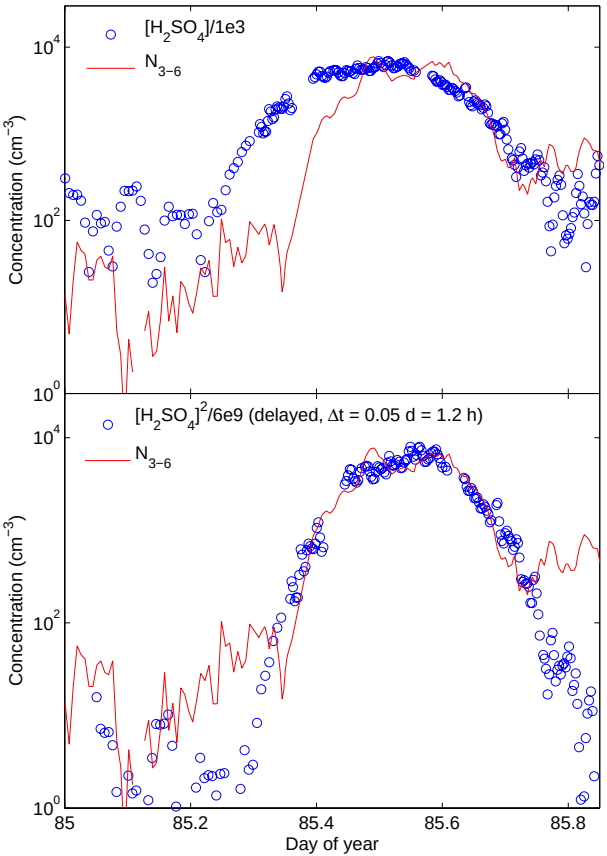

Fig. 2. (a) (upper panel) Number concentration of 3–6 nm particles (N_{3-6}) and sulphuric acid concentration (scaled) for day 85 (26 March 2003). (lower panel) N_{3-6} and $[H_2SO_4]^2$ (scaled) delayed by the time shift Δt=1.2 h, showing clear correlation between N_{3-6} and $[H_2SO_4]^2$ during the event.

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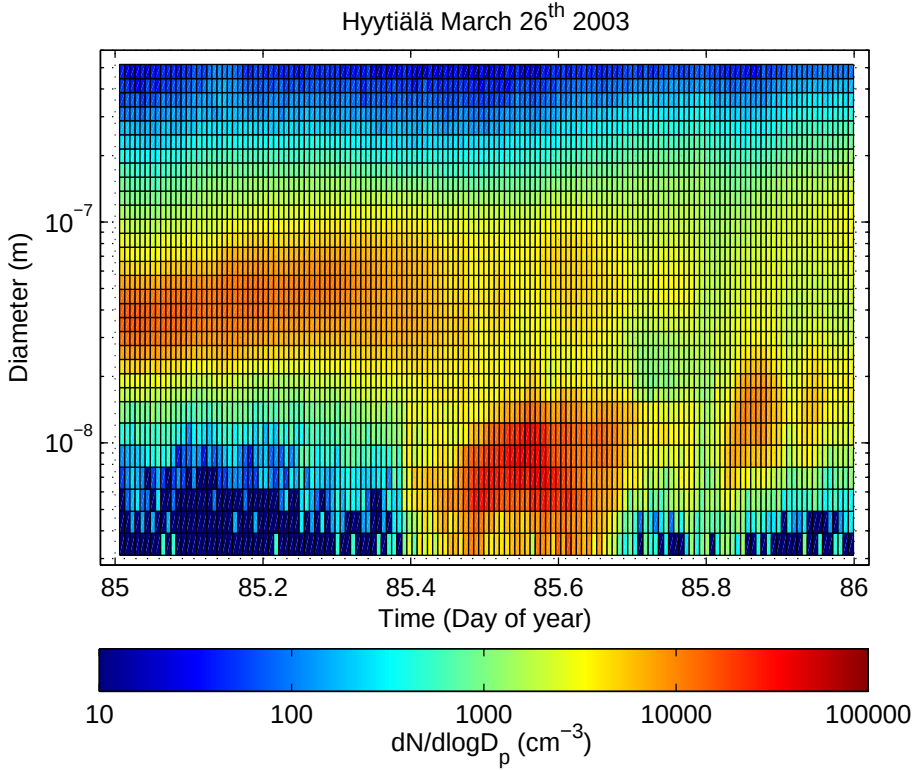

Fig. 2. (b) Surface plot showing the time evolution of particle size distribution on day 85 (26 March 2003) measured by DMPS. Time is on the x-axis, particle diameter on the y-axis and colour indicates normalized number concentration.

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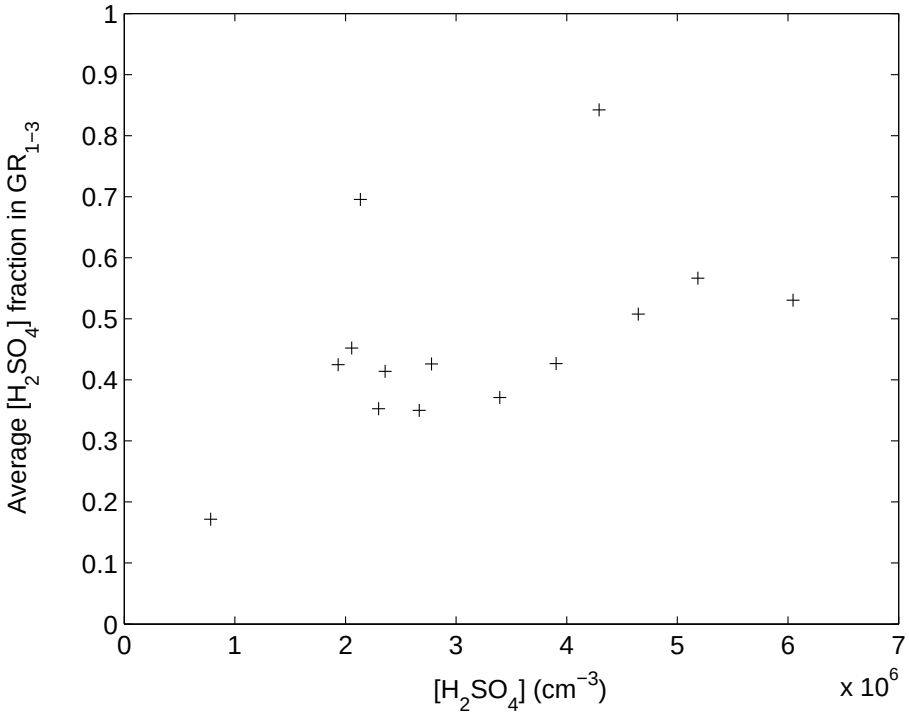

Fig. 3. Average contribution of sulphuric acid to growth from 1 nm to 3 nm as a function of sulphuric acid concentration on event days during QUEST 2 campaign. One point represents average on one day from 09:00 a.m. to 03:00 p.m. A point at $[H_2SO_4]=9\times10^6\,cm^{-3}$ for which $[H_2SO_4]$ can explain the growth completely is not indicated in the figure.

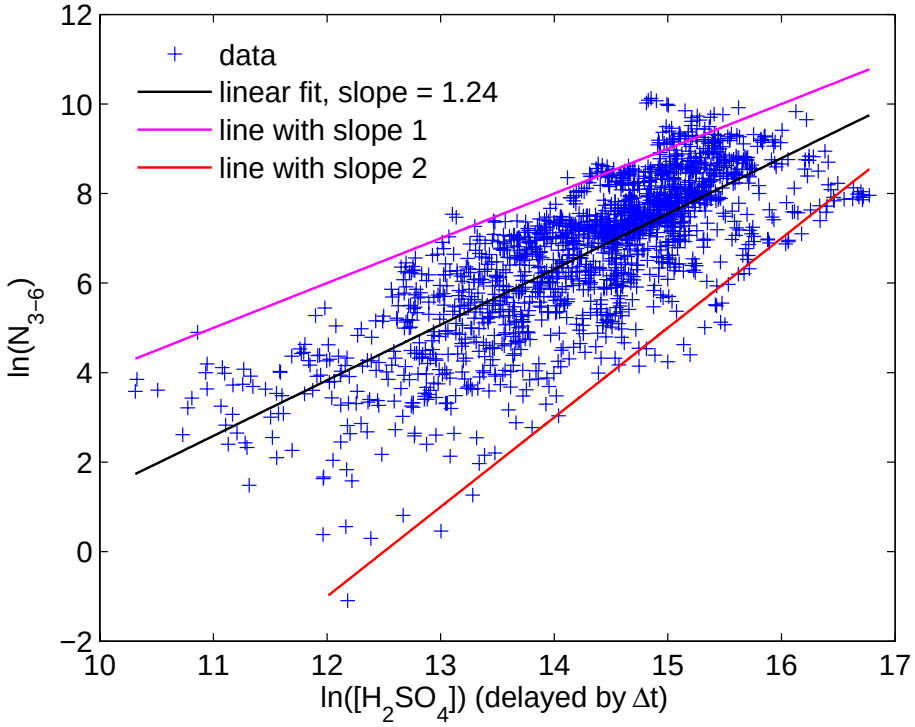

Fig. 4. Number concentration of 3–6 nm particles (N_{3-6}) as a function of sulphuric acid concentration during particle formation events. The time shift between N_{3-6} and $[H_2SO_4]$ has been taken into account by delaying $[H_2SO_4]$ by Δt. Linear fit to the data by the method of least squares and lines corresponding relationships N_{3-6}~$[H_2SO_4]$ and N_{3-6}~$[H_2SO_4]^2$ are shown.

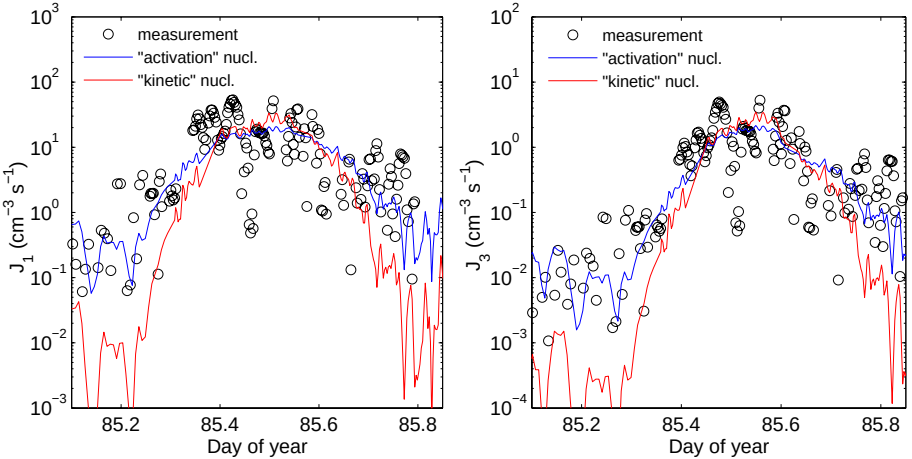

Fig. 5. Nucleation rate (J_1, left panel) and formation rate of 3 nm particles (J_3, right panel) on day 85 (26 March 2003) estimated from measurements and calculated from sulphuric acid concentration using two hypothetic nucleation mechanisms: “activation type” and “kinetic type” nucleation.

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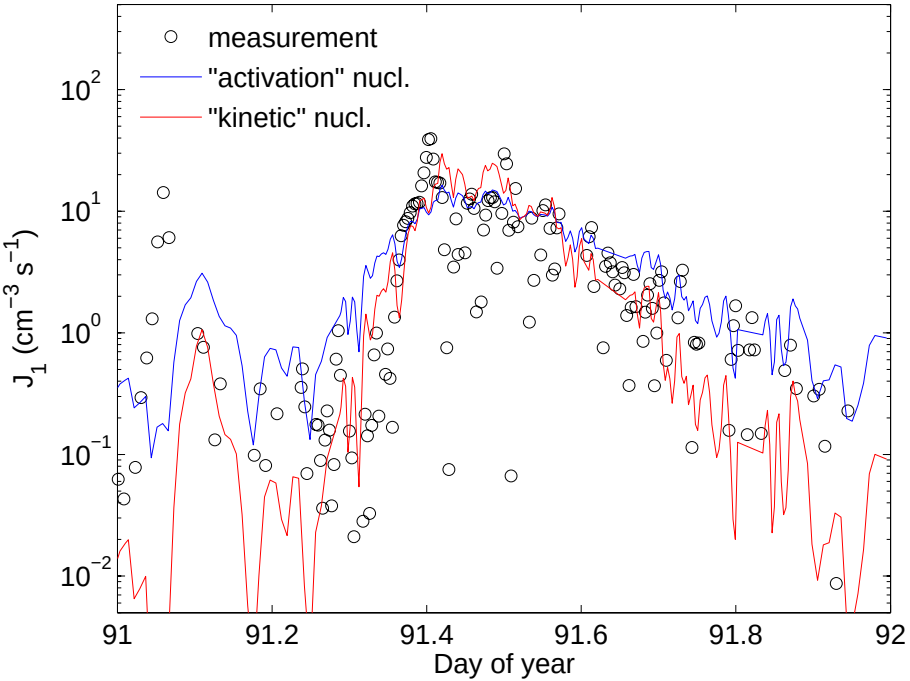

Fig. 6. Nucleation rate on day 91 (1 April 2003) estimated from measurements and calculated from sulphuric acid concentration using two hypothetic nucleation mechanisms: “activation type” and “kinetic type” nucleation.

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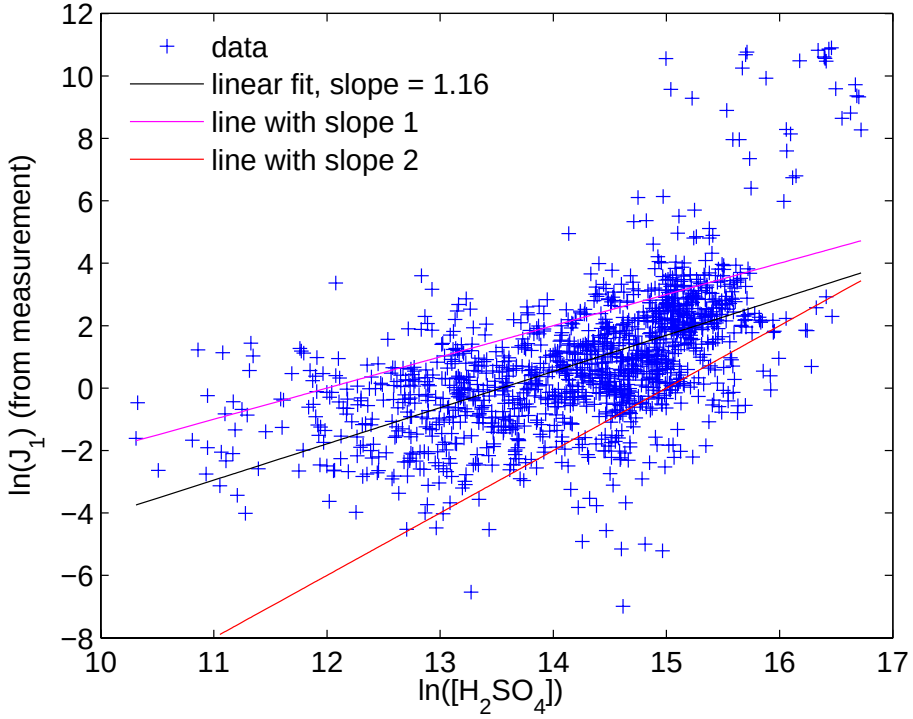

Fig. 7. Logarithm of nucleation rate J_1 estimated from particle measurements versus logarithm of sulphuric acid concentration.

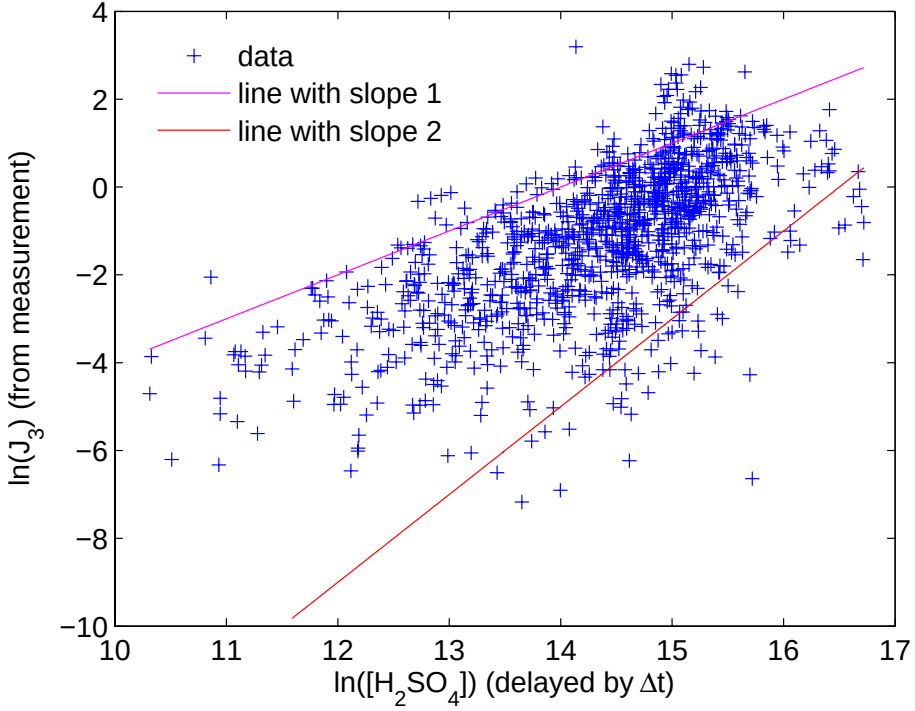

Fig. 8. Logarithm of formation rate J_3 estimated from particle measurements versus logarithm of sulphuric acid concentration. Sulphuric acid concentration has been delayed by Δt, i.e. value $J_3(t)$ has been associated with value $[H_2SO_4](t\text{-}\Delta t)$.